Art. XV.—*A Contribution to the Theory of Gel Structure.*

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It is now generally admitted that a gel is a diphasic system, but divergent views are held concerning the nature and possible vectorial characteristic of the more solid phase, and the forces which hold the more liquid phase in position. Whether the meshwork of the more solid phase is composed of micro-crystals, or is truly amorphous, or whether both can give rise to gel structure, further refinements in ultra-microscopy may determine. But whatever view may be correct, the question is unaffected, whether the "filaments," "needles," or micellae assume a definite arrangement under the influence of forces akin to those that produce crystallisation. Is the meshwork of the more solid phase devoid of any vectorial characteristic, or is such actually present?

To throw some light on this problem I commenced certain experiments in 1909 on the shapes of bubbles found in strong gelatine gels when decompressed after being subjected, when warm and during setting, to gas under pressure—generally CO_2. The ordinary fracture of a gel can be described as "perfectly conchoidal," and this in itself indicates that like obsidian or ordinary flint homogeneity of structure may be present. But such reasoning cannot be pushed very far, for conchoidal fracture can be given by crystalline substances, notably quartz. It was this consideration that led me to examine the internal fractures produced by bubble formation. The simplest way to carry out the experiment is to subject warm 10% gelatine solution in a sparklet syphon to the action of CO_2 under pressure. I have also employed the Leonard Hill high pressure chamber with gas pressures of 10-20 atmospheres but the small quantity of gelatine that can be used is here a disadvantage. On decompression the appearance of the jelly is remarkable. Each bubble that forms is lenticular, or apparently a disk of great thinness, and entirely in one plane. I communicated this result to the late Mr. William Sutherland, and he wrote me as follows, under date May 7th, 1910;—

"The form of the gas cavity will depend on the rigidity of the jelly in the following way: The spherical form characteristic of

bubbles in a liquid, when they are small, results from the equality of hydrostatic pressure in all directions. But in a jelly suppose a cavity of any arbitrary shape formed. In the jelly bounding it there will be surface stresses due to the unequal pressure effects of the surface tension acting on parts of the surface of different curvature. If the jelly is weak enough it will begin to flow (like lead in the manufacture of pipes), and will assume finally the spherical form round the cavity. But if the jelly is too strong to flow quickly enough the unequalites of stress will not be relieved rapidly. The escape of gas may accentuate them, with the result that in a stiff enough jelly the material begins to tear at the part of the original arbitrary cavity, where the conditions are most favourable, and the tearing will go on till no longer necessary. A slow flow of the jelly will round off the edges of the spreading cavity, and give it a lenticular shape."

The bubbles make all possible angles with each other, giving a spangled appearance. This point I was particularly anxious to investigate. In a recent number of "Science Progress,"[1] there is a reference to an article by Hatschek in 1914, which apparently dealt with this same subject—the formation of bubbles in jellies. I have been unable through the war to get Hatschek's article in the "Kolloid-Zeitschrift," and so cannot institute any comparison between his results and mine, but most certainly my observations did not support the assumption that any particular angle was predominant amongst these disk-like bubbles. I was at first inclined to regard these results as evidences of the absence of crystalline or pseudo-crystalline arrangement; but as lines of cleavage are absent in certain substances most definitely crystalline, this view can not be rigidly held. If, however, a vectorial characteristic is present, the arrangement must be similar to that exhibited in masonry composed of courses of uniform cubical bricks.

Fracture and Regelation.

If a solid cylinder of 5%-10% gelatine is broken transversely at any point, and the fracture mended by warming the opposing surfaces and allowing to set, it will be generally found that the former line of fracture is the seat of weakness. If a straight piece of combustion tubing filled with 10% jelly is heated between cork guards at some point, and then allowed to stand over-night, it will

1 S. C. Bradford. On the Gelation of the Natural Emulsoids. Science Progress, July, 1917 p. 64.

be found that on expelling the jelly (which can be done with a little practice by quick immersion of the whole tube in warm water) the place of former heating is weak, and fractures readily. Indeed, this region may look to the eye actually thinner. The cause of this is to be found in the well-known hysteresis of jelly. That part which is heated and allowed to reset, will melt more readily on the application of the warmth necessary to loosen the jelly cylinder in the tube. But if a cylinder of jelly is cut through slowly with a platinum wire, carrying an adjustable electric current just sufficient to produce melting of the jelly, a complete transverse lesion can be obtained, which on resetting exhibits no weakness. If an ordered arrangement of the solid phase was pronounced, one would expect to find weakness always manifest, when continuity was once disturbed. No definite conclusion can be based on this evidence, but once more it points either to the lack of any vectorial character or to such being of the nature of a complex of uniform cubical or rectangular units.

The Struve-Baumstark Phenonemon.

In 1885 a method was described by F. Baumstark[1] of preparing aqueous extracts of brain tissue for purpose of analysis. The procedure was simply to immerse the brain matter in ether, whereupon after a day or two a copious watery extract was expelled from the brain tissue, and collected at the bottom of the receptacle. Baumstark found that petroleum ether was without this effect. In reality this phenomenon had been already observed and utilised in 1876 by H. Struve,[2] who investigated the watery extract obtained from various plant and animal tissues. The same device was resorted to by MacMunn[3] in order to obtain muscle extracts for the study of myohaematin.

I have made a number of experiments on this method, chiefly from the standpoint of the structure of gels.

One hundred grms. sheep's brain, immersed in wet ether, gave in three days 37.5 cc. aqueous extract. After one week the amount was 39.9 cc; after three weeks 41.4. The solid matter in this extract was 3.6%.

One hundred grms. of meat fairly fat-free gave in one week 17.5 cc. extract. The solid matter was 4.2%.

1 Zeit. f. physiol. Chemie. Vol. *9*, p. 145. 1885.
2 Bull. de l'Acad. Imp. de St. Petersburg. Vol. *21*, p. 243. 1876.
Also Bericht. deutsch. chem. Gesell. Vol. *9*, p. 623. 1876.
3 Journal of Physiol. Vol. *8*, p. 54. 1887.

One hundred grms. of the same, finely minced, gave the same amount, namely, 17.5 cc. extract. Solid matter = 4.5%. If brain or muscle be exposed merely to ether vapour, a "sweating" takes place, and drops of extract are formed, but one never obtains anything like the quantity of fluid as when the tissue is immersed in the ether.

Two hundred grms. dry sand in a separating funnel when wetted with tap water retained, after dripping had ceased, 48.5 cc. water.

On pouring ether vapour on the surface of the sand 4 cc. water were immediately discharged below. If the ether vapour is admitted to the under surface only of the sand, this discharge does not take place.

If instead of vapour a quantity of liquid ether is poured on the surface of the wet sand, the following events occur:—At first a few cc's. of water, then a further quick flow of water holding increasing amounts of ether in solution, then ether charged with water, and, lastly, ether with a very small quantity of dissolved water. The sand will now be found to be wet with ether. If petroleum ether is used, then only a small quantity of fluid is very slowly discharged.

A given quantity of sand will hold more tap water than it will water which has been shaken with ether.

It is obvious that we have two effects here. One is the sudden lowering of surface tension due to solution of ether, and consequent fall of the capillary columns of water between the sand grains. If water is allowed to mount up a capillary tube and a small drop of ether is placed in an enlarged part above, but not blocking the lumen, then as soon as the vapour falls down the capillary a rapid drop in the water meniscus can be seen. The other effect is the progressive solution of the ether in the water, the augmentation of the latter in volume and hence progressive discharge until the ether displants the aqueous phase. At the same time there may be diminution of "Haftdruck" in the sense of Traube.[1]

Now coming to gels, we find that some give the Struve-Baumstark reaction, and others do not. Amongst those that display this property in a marked degree are the soaps. A 10% sodium stearate (Merck) gel placed in ether begins to discharge liquid at once. If the fluid is drained off until no more forms, it will be found

1 Theorie des Haftdruckes, etc. Biochem. Zeit. Vol. 54, p. 305. 1913.

that the liquid phase of the soap gel has been replaced wholly by ether (containing, of course, some water in solution). The gel now exudes ether on compression, and if lit will burn violently. The discharged fluid, however, has some of the solid phase in solution, for it contains more than double the amount of solid matter present in the fluid expressible from the original gel, and moreover, if exposed to the air, and so allowed to lose its dissolved ether, will revert to a moderately firm jelly. Indeed this seems to me to be an ideal method for studying stages of gel formation, as the process can be made slow or rapid as desired. I had at first attributed this partial solution of the solid phase to the presence of alcohol, but repeated washing with water failed to remove this faculty from the ether. The ether layer above the soap jelly in these experiments was found to contain some solid matter in solution, and from the qualitative tests I employed this seemed to be fatty, acid, but I have been unable to pursue this particular investigation.

The discharged fluid will set, therefore, on exposure to the air, and the gel thus formed can be once more subjected to ether; the liquid phase and a portion of the solid dissolved in it will be discharged and the remainder of the solid phase left behind impregnated with ether. This procedure can be repeated three or four times.

The fact that the liquid phase of the soap can be discharged and be replaced by ether is obviously similar to that obtained with wet sand. It certainly indicates that the liquid phase of the soap gel is held by capillarity in the open meshwork of the solid phase.

If, however, a 5% gelatine gel is submitted to ether immersion no fluid, or only an exceedingly small amount is extruded. Whereas a 2% gelatine will show the Struve-Baumstark phenomenon clearly. That there exists a profound physical distinction between these two is evident to the sense of touch alone—the 5% gelatine is dry, the 2% is wet. In the 5%, and in greater concentration, the fluid, we may assume, is not merely held by capillarity, but exists in solid solution in the substance of the framework, whereas in the 2% gel the water-logged lattice holds by capillarity a fluid with a small amount of solid matter in solution. This is at any rate an explanation that falls in with modern physico-chemical theories of gelation. Another possible hypothesis is that the liquid phase in the more rigid gels is formed of small vesicles completely enclosed by walls of solid phase in honey-comb fashion. This explanation is, however, rendered most unlikely by the results of ultra-

microscopic examination.[1] In egg-white coagulated by heat, we have a gel containing some 86% water, but no fluid is extruded when the coagulum is subjected to ether. It is just likely that we have a honey-comb structure here, though the hydrophile nature of the framework may also take its part. On the other hand, the thallus of laminaria, as Struve discovered, exudes fluid copiously. A silicic acid gel containing 13.4% solid matter, though easily fractured, did not give a positive result.

It seems to me, therefore, that the Struve-Baumstark phenomenon can be employed to distinguish those gels where the liquid phase is held, in part at least, by capillarity from those in which the fluid is held, through imbibition, by the hydrophile lattice of the solid phase.

1 See for instance, W. H. Howell: Structure of the Fibrin-Gel and Theories of Gel Formation. American Journ. of Physiol. Vol. 40, p. 526. 1916.